

Supercritical Fluids

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Chapter 13

Supercritical Fluid Adsorption at the Gas-Solid Interface

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Adsorption of a supercritical fluid upon the surface of an adsorbent significantly alters the gas-solid interface thereby permitting the removal and migration of bound adsorbates. Such a process can contribute substantially to the regeneration of adsorbents and the chromatographic separation of solutes as reported in the scientific and patent literature. In this paper, we have characterized the adsorption of dense gases at solid interfaces in terms of their reported adsorption isotherms. Particular emphasis has been placed on the pressure at which maximum differential adsorption of the gas occurs and its importance in assuring rapid breakthrough of sorbates from packed columns. An experimental approach is presented for determining adsorbate breakthrough volumes as a function of gas compression using elution pulse chromatographic techniques. The derived retention volume data define distinct regions of solute breakthrough characteristics which are determined by the relative uptake of the compressed fluid on the sorbent surface. The results obtained in this study permit an estimation of the physical conditions required to effectively remove aliphatic and aromatic hydrocarbons from such sorbents as alumina and porous organic resins with minimal compression of the supercritical fluid phase.

The utilization of supercritical fluids in conjunction with adsorbents and active solids is well documented in the technical literature. The most frequently cited applications involve the use of dense gases for the regeneration of adsorbents (1) and as mobile phases in supercritical fluid chromatography (2). Numerous

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patents also contain examples of the removal of specific solutes, such as caffeine or nicotine, from supercritical fluid media by activated carbon (3, 4) and ion exchange resins (5, 6). Fractionation of solutes from dense gas streams has also been demonstrated by Barton and Hajnik (7) utilizing molecular sieves as a sorbent. Less well known, but of historical importance, is the sorption of methane by coal (8), an equilibria of importance in preventing mine explosions. Recently, Findenegg (9) has suggested that radioactive gases may be stored to advantage on zeolites at elevated pressures.

Regeneration of adsorbents was initially demonstrated in the mid-1970's in both Japan (10) and the United States (11, 12). In research sponsored by the Environmental Protection Agency (13-15), Critical Fluid Systems, Inc. (Arthur D. Little) demonstrated the feasibility of regenerating activated carbon and organic resins using supercritical carbon dioxide. Typical conditions in the above studies utilizing CO₂ for the removal of selected sorbates from activated carbon are shown on a plot of reduced state in Figure 1. For the extractions cited, a wide range of reduced temperature and pressure have been employed depending upon the chemical nature of the compounds being desorbed. Presumably, these regeneration conditions were selected empirically or are based on independent measurements of sorbate (solute) solubility in the supercritical fluid.

More recently, Kander and Paulaitis (16) have studied the adsorption of phenol onto activated carbon and measured its sorption equilibria from dense CO₂. These researchers found that temperature controlled the adsorption equilibria and that phenol uptake was negligibly effected by changes in the gas phase density. Such a result indicates that factors other than a solute's solubility in a dense gas play a key role in defining the adsorption equilibrium which accompany such processes.

There is a synergism between adsorption and chromatographic processes which is clearly demonstrated in the supercritical fluid literature. Research in supercritical fluid chromatography can usually be divided into analytical applications and the measurement of physicochemical data. Early analytical separations methodology performed at pressures close to ambient conditions showed that the elution order of injected solutes could be altered by changing the nature of the carrier gas (17-20). Later, adsorbents and crosslinked polymeric packings were utilized in analytical studies to circumvent the problem of stationary phase volatility in the highly compressed carrier gas. For example, Sie and Rijnders (21, 22) demonstrated the advantages of using such adsorbents as alumina and microporous polymers for fractionating a wide variety of mixtures including polycyclic aromatics hydrocarbons, alkaloids, and epoxy resin oligomers. Results obtained in the above study indicated that the solute distribution coefficients could be varied as a function of carrier gas pressure in a rather dramatic fashion and that elution peak shape was substantially modified by the interaction of the supercritical fluid with the sorbent surface. Kobayashi and co-workers (23-28) using tracer perturbation chromatography have substantiated the above findings and determined equilibrium K-values, isotherms, and thermodynamic functions of adsorption for light hydrocarbons on several adsorbents.

In this paper, we have utilized literature data in tandem with pulse chromatographic measurements to define the role of supercritical fluid adsorption at the gas-solid interface. It should be appreciated that the adsorption of the supercritical fluid on the adsorbent surface is appreciable at higher pressures leading to the formation of a condensed phase (29) in the microporous adsorbents commonly used in regeneration experiments. The formation of such a "liquid-like" film at the interface can have a profound effect in determining the uptake of another adsorbate at the solid surface or in the conditions required for regeneration of the adsorbent surface. The measurements reported in this study extend out to 1600 atmospheres, a compression regime previously unexplored by gas-solid chromatography. Such experiments have permitted us to correlate chromatographic retention volume measurements with adsorbate breakthrough characteristics as a function of pressure for several adsorbent/adsorbate systems. The role of the supercritical fluid at the gas-solid interface has been invoked to explain these breakthrough characteristics, therefore a brief discussion of the fundamentals governing the adsorption of high pressure gases at the adsorbent interface will be given.

Fundamentals of Supercritical Fluid Adsorption

Fundamental studies on the adsorption of supercritical fluids at the gas-solid interface are rarely cited in the supercritical fluid extraction literature. This is most unfortunate since equilibrium shifts induced by gas phase non-ideality in multiphase systems can rarely be totally attributed to solute solubility in the supercritical fluid phase. The partitioning of an adsorbed specie between the interface and gaseous phase can be governed by a complex array of molecular interactions which depend on the relative intensity of the adsorbate-adsorbent interactions, adsorbate-adsorbate association, the sorption of the supercritical fluid at the solid interface, and the solubility of the sorbate in the critical fluid. As we shall demonstrate, competitive adsorption between the sorbate and the supercritical fluid at the gas-solid interface is a significant mechanism which should be considered in the proper design of adsorption/desorption methods which incorporate dense gases as one of the active phases.

In general, adsorption of a high pressure gas follows a Type II BET isotherm. The shape of the isotherm is partly dependent on the units chosen for the isotherm coordinates, however there is a major difference in the character of the isotherm depending on whether absolute or Gibb's adsorption is chosen for the abscissa. Whereas absolute adsorption is a measure of the total mass or volume of the gas adsorbed onto the surface, Gibb's adsorption (or the surface excess) measures the amount of gas adsorbed on the solid surface in excess of that corresponding to the density of gas in the fluid phase at the same temperature and pressure. This latter definition provides some insight as to the molecular interactions taking place at the interface as a function of gas density. A typical adsorption isotherm illustrating both the absolute and differential (Gibbs) adsorption is shown in Figure 2.

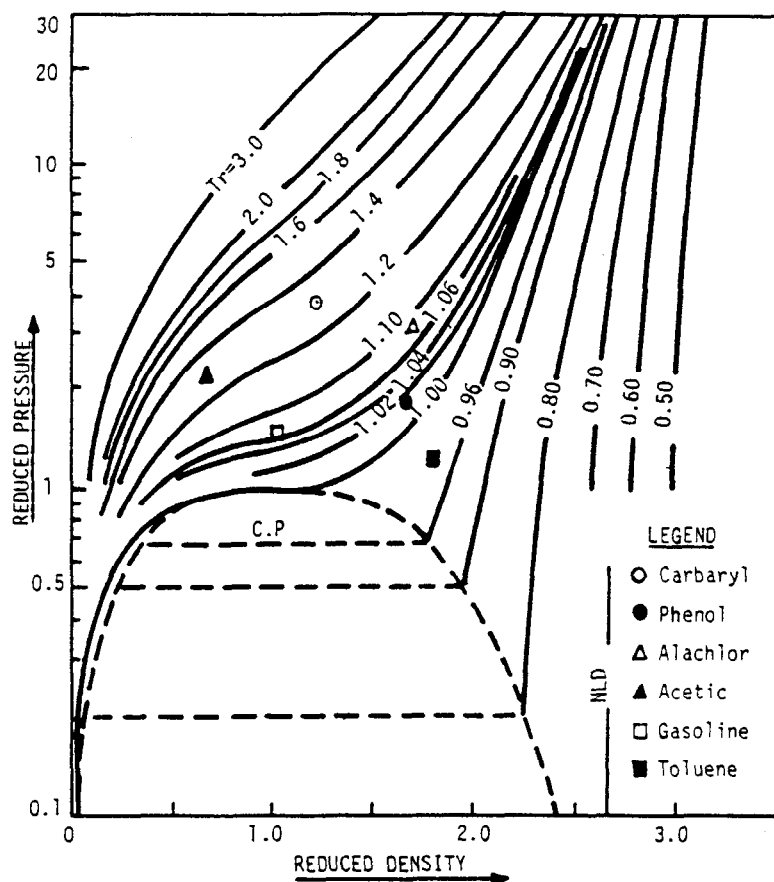


Figure 1. Reported conditions for the supercritical fluid desorption of selected adsorbates from activated carbon.

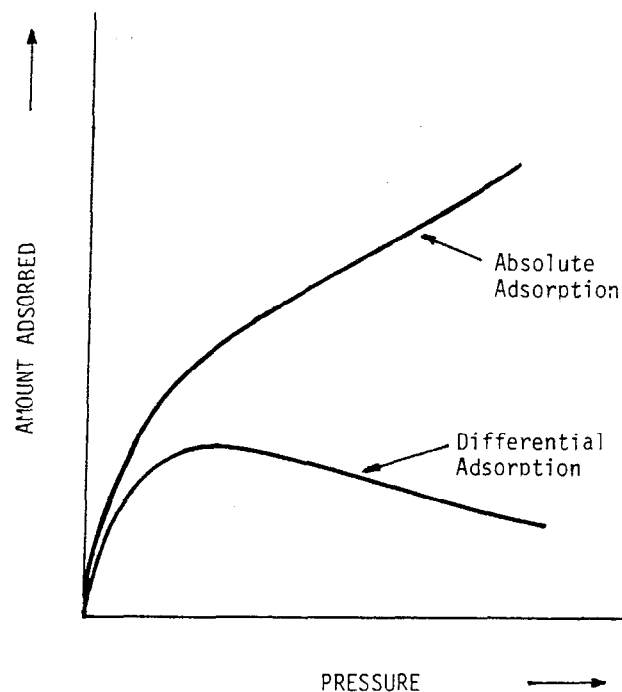


Figure 2. Typical adsorption isotherm for a supercritical gas in which absolute and differential adsorption are express as a function of pressure.

Menon has noted in his comprehensive review (30) that an adsorption maxima occurs as a specific gas pressure, p_{\max} , when the Gibbs adsorption is plotted versus the gas pressure. These adsorption maxima are quite pronounced when the supercritical fluid is adsorbed at reduced temperatures approaching unity. Further compression of the critical fluid beyond p_{\max} results in a density increase of the adsorbed film and a concomitant decrease in the surface excess as the gas phase approaches a density equal to or exceeding that of the adsorbed phase. As we shall show later, attainment of this specific pressure value is critical for saturating the adsorbent surface with the compressed fluid and thereby leading to conditions which favor the desorption of the bound solute from the surface region. Menon (31) has correlated the occurrence of p_{\max} for various gases in terms of their respective critical properties and has proposed the following empirical equation which is applicable for adsorption on macroporous adsorbents (pore diameters greater than 20 Å):

$$p_{\max} = P_c T_r^2 \quad (1)$$

where P_c = critical pressure of the gas

T_r^c = reduced temperature at which adsorption occurs

The above relationship predicts a monotonic increase in p_{\max} with increasing temperature as shown in Figure 3 for three different gases. Hence, the maximum amount of gas (by the Gibbs definition) adsorbed on the surface of the adsorbent can be attained at a lower pressure by operating close to the critical temperature of the adsorbed gas. Application of even higher pressures than p_{\max} will result in a large increase in the cohesional energy of the adsorbed gas leading to the formation of a liquid-like layer on the surface of the porous adsorbent (27).

Additional studies by Menon (32) have indicated the p_{\max} can occur at lower pressures than those predicted by Equation 1 depending on the pore structure associated with the adsorbent. Empirically, adsorbents possessing microporosity exhibit a p_{\max} that is 0.6-0.8 of the value predicted by Equation 1. This observation is attributed to the overlapping of potential fields in the adsorbent pores, thereby enhancing sorption of the gas at lower pressures. Experimental studies by Ozawa (33) have verified this trend as shown in Figure 4 for the CO₂/activated carbon system. Here the adsorption maxima for the gas occurs at a lower pressure than the critical pressure of carbon dioxide. It should also be noted that the amount of gas adsorbed is decreased at higher reduced temperatures and that additional compression is required to reach a defined adsorption maxima (i.e., at very high values of T_r it is sometimes difficult to discern a well-defined adsorption maximum). The above trend has also been found for other adsorbent/adsorbate systems, such as silica gel/CO₂.

The dependence of gas adsorption on the pore structure of the sorbent has been extensively studied by Ozawa, Kusumi, and Ogino (34) and theoretically correlated by application of the Pickett equation. Data obtained from this study has been plotted

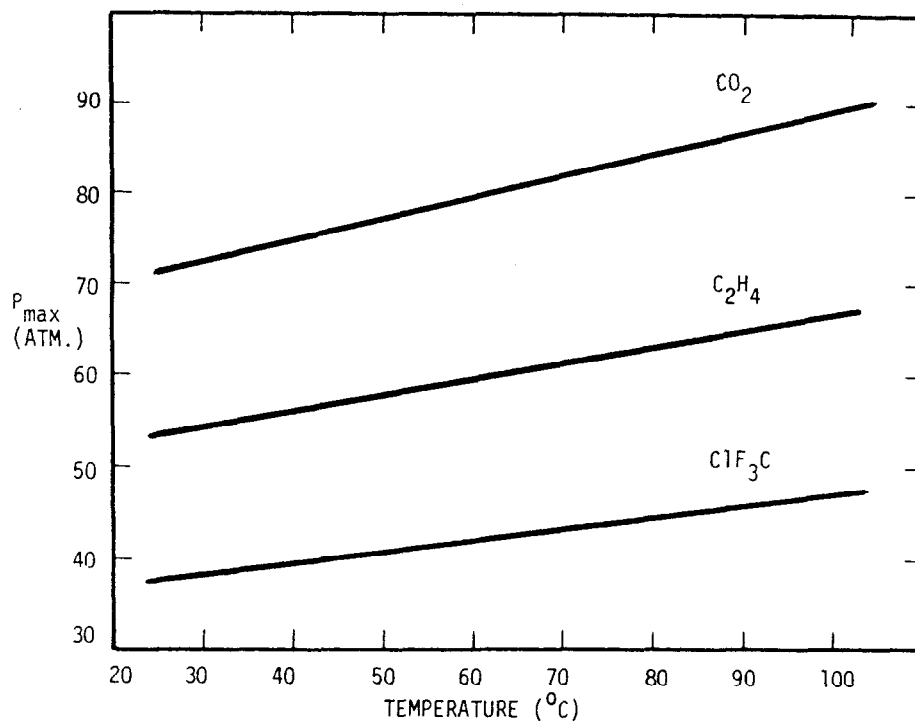


Figure 3. Dependence of p_{\max} on temperature for various gases according to Menon (30) on macroporous adsorbent.

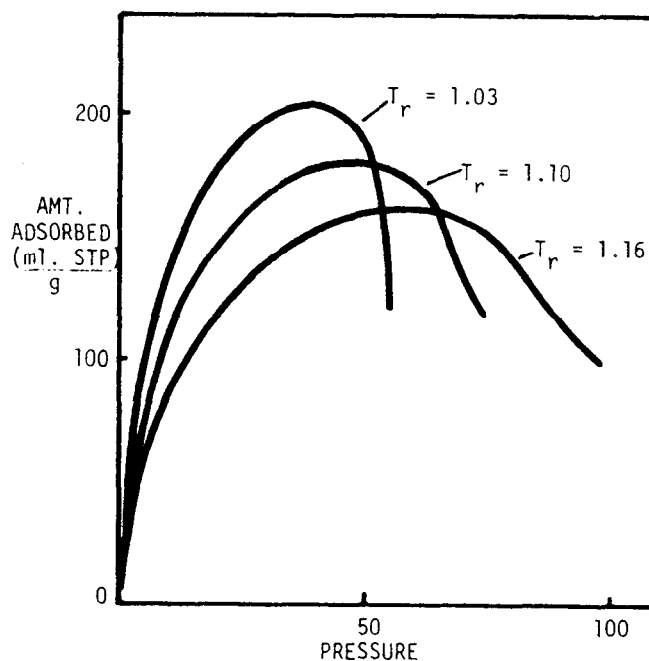


Figure 4. Adsorption isotherms for the carbon dioxide/activated carbon system. Reproduced with permission from Ref. 33. Copyright 1972, Chemical Society of Japan.

in Figure 5 where the p_{\max} value versus the mean pore diameter of the adsorbent (activated carbon) is shown for CO_2 sorption. The adsorption maxima in this case, increases with increasing pore diameter, asymptotically approaching a constant value at large pore diameters. The value predicted by Menon's relationship (Equation 1) has also been included for the purpose of comparison. Although it would seem prudent to utilize an adsorbent of low porosity to avoid additional gas compression, mitigating factors such as adsorption capacity and stereo-selectivity also play a seminal role in the final selection of a suitable adsorbent. The pore size dependence of p_{\max} at various temperatures has also been verified for above carbons and shows a similar dependence to that exhibited in Figure 3.

Further discussion on the theoretical aspects of supercritical fluid adsorption on solids can be found by consulting the papers of Findenegg (35-37). The importance of the high pressure adsorption maximum as discussed above becomes apparent if we compare typical p_{\max} values on a plot of reduced state variables with conditions that are commonly employed for the regeneration of adsorbents (Figure 1). As shown in Figure 6, p_{\max} values for CO_2 on typical carbonaceous adsorbents occur at considerably lower reduced pressures ($p_r = 0.5-1.0$) than those utilized for the desorption of common organic solutes (14) or pesticides (1). This result implies that potentially much lower pressures and volumes of supercritical CO_2 could be used to displace adsorbed solutes from the adsorbent surface by maximizing the competitive adsorption of the dense CO_2 on the solid surface.

To provide some experimental verification of the above hypothesis, we have measured via pulse elution chromatography, breakthrough volumes (the peak maximum retention volume in linear elution chromatography corresponding to the 50% breakthrough volume in frontal analysis) of model adsorbates on two different adsorbents over an extended pressure range using CO_2 as the critical fluid. Our experimental results suggest that there are distinct regions in which the surface of the adsorbent is undergoing modification due to the adsorption of the supercritical fluid carrier gas. The implications of these results have permitted the identification of distinct pressure ranges which can be used for the fractionation of dissolved moieties in the critical fluid, a minimum pressure which should be attained for commencement of adsorbent regeneration, and an upper pressure limit at which sorbate breakthrough volume becomes constant with increasing pressure.

Experimental Measurements

The experimental apparatus utilized for these studies is of similar design to that reported by Giddings, Myers, and King (38) as is depicted in Figure 7. Compression of the mobile phase was accomplished using an Aminco air-actuated diaphragm compressor which was kept in a heated chamber above the critical temperature of the carrier gas. Pump pulsations and flow irregularities were minimized by storing the compressed fluid in a high pressure ballast chamber which served as a source of mobile phase. Pressures up to 3000 psig were adjusted by using

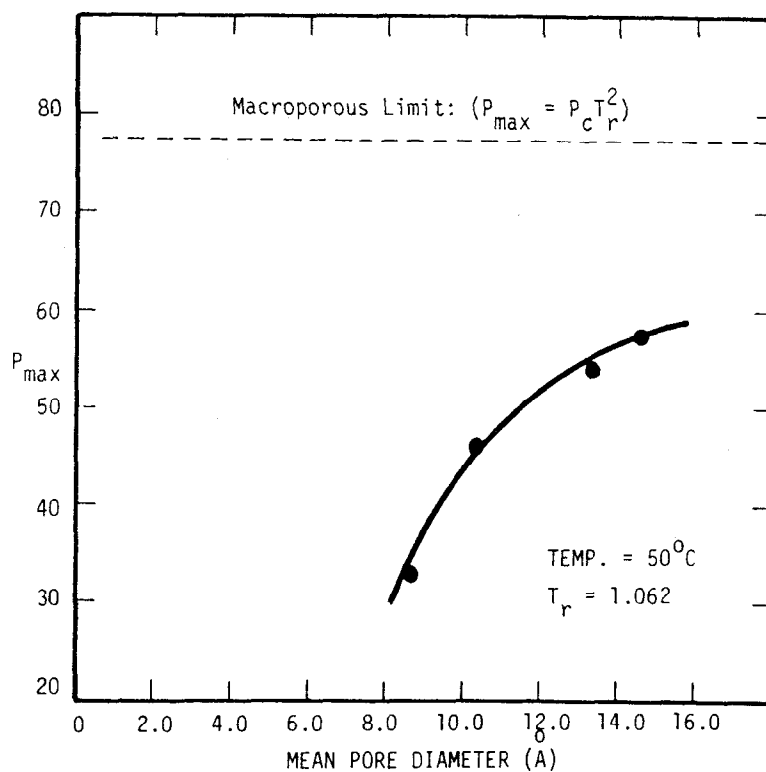


Figure 5. Relationship between the pressure at which maximum differential adsorption of carbon dioxide occurs and the mean pore diameter of activated carbons.

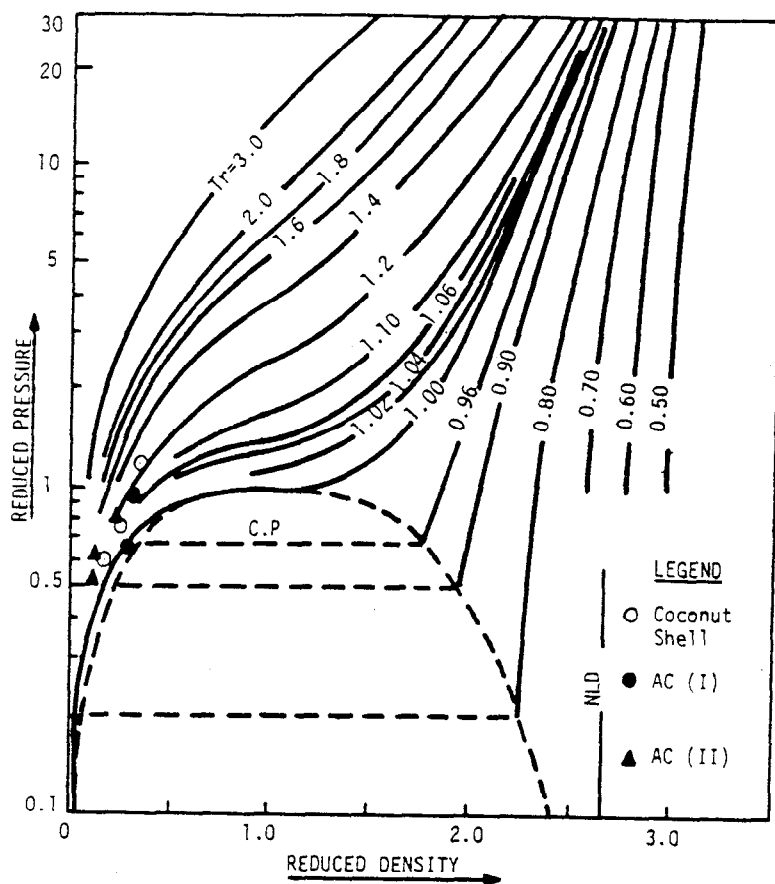


Figure 6. Reported adsorption maxima for carbon dioxide/adsorbent system on a plot of reduced state. (I) and (II) represent different types of activated carbon (AC).

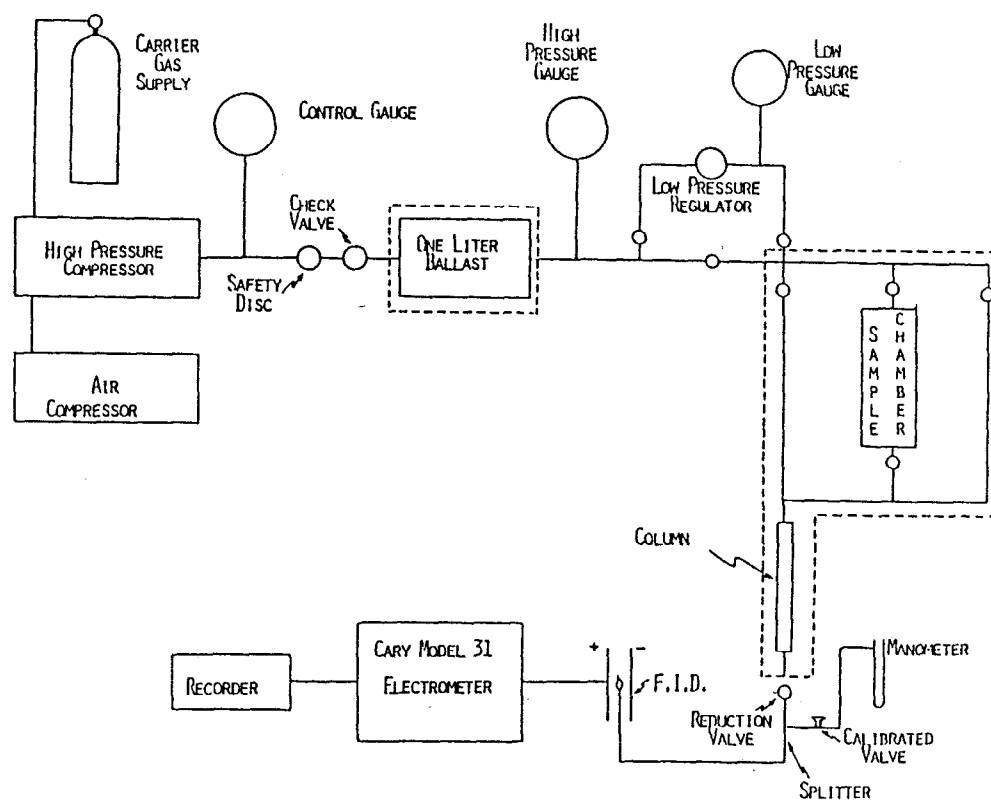


Figure 7. Experimental high pressure gas chromatographic apparatus for retention volume measurements.

an Apco backpressure regulator in conjunction with a Bourdon tube gauge. Regulation of pressures beyond 3000 psig was achieved by isolating the low pressure gauge from the main flow system and subsequently regulating the entire chromatographic system with a dual contact electrical control gauge (modified Aminco Model 47-18330). The sampling chamber/valve and column were placed in a heated, thermostatted oven held at 40°C (dashed line in Figure 7).

Column design and preparation incorporated previously described methods reported in the literature (39). Two different adsorbents were employed: a 100/120 mesh crosslinked styrene/divinylbenzene resin (Polypak P-Waters Associates) and a Woelm aniontropic activity grade alumina. These adsorbents were packed in 300 and 94 cm. stainless steel columns having a 1 mm. internal diameter. Pressure drop across the adsorbent bed was kept to a minimum (<0.02 atm.) by using a heated pressure reduction valve at the end of the column. Typical linear flow velocities through the columns were in the range of 0.27-2.17 cm/sec.

Pneumatic transport of the solute after decompression at the end of the column to the detector orifice was facilitated by application of a heating tape to a small length of narrow bore tubing. Detection of the solute elution profile was accomplished using a fabricated, non-commercial flame ionization detector. Flow rates of the carrier gas were adjusted under ambient conditions by calibrating a U-tube manometer in terms of gas flow rate. This required opening the carrier gas flow splitter so as to divert the entire flow through the detector orifice, subsequently measuring the flow rate and differential pressure on the manometer, and then returning the calibrated metering valve to its initial setting to reestablish the split (1:6-1:10) of the carrier gas flow. Calibration with and without the detector gases (air & H_2) revealed the absence of any backpressure effect due to the detector combustion gases.

Experimental assessment of the column void volume proved to be critical since the solute retention volume approaches the void volume as pressure is increased. Following the recommendations of Kobayashi (24), we used an unretained solute, methane, for this measurement. Values for the void volume determined over an extended pressure range were 1.8 and 0.5 ml. for the crosslinked resin and alumina columns, respectively. These figures were in excellent agreement with void volume approximations of 1.4 and 0.45 ml. based upon the geometric volume of the column assuming a porosity of 0.6 for the packed beds.

The adsorbates and adsorbents in this study were chosen to reflect a range of different types of molecular interactions as well as to observe whether the retention volume data trends could be generalized. In addition, solutes were picked which would rapidly equilibrate with the chosen adsorbents (no hysteresis) and whose distribution coefficients could be measured conveniently over as wide a pressure range as possible. As shown in Table I, the adsorbents corresponded to two distinctly different chemical types as classified by the criterion of Kiselev (40). The alumina represented an adsorbent capable of specific interactions with sorbates having localized peripheral

electron density, since it possesses a localized positive charge on its surface. The crosslinked organic polymer is a Type III adsorbent since its negative charge on the surface is due to the presence of an aromatic pi-electron system within its molecular structure. The adsorbates employed represented a homologous series of n-alkanes (Group A sorbates) and two Group B adsorbates, benzene and naphthalene, which have peripheral pi-electron density.

Table I. Adsorbent/Adsorbate Classes
Utilized in the Chromatographic Experiments

Adsorbent Type	Adsorbate Type
Al ₂ O ₃ (Type I)	n-Pentane n-Hexane (Group A) n-Heptane
Styrene/Divinylbenzene Resin (Type 2)	Benzene Naphthalene (Group B)

Data Reduction

There is a fundamental relationship described in chromatographic theory between the retention volume of a elution peak and the mid-point of a breakthrough curve achieved by operating the column under frontal analysis conditions (41). In the Henry's Law region of the adsorption isotherm, the net retention volume and its measurement can be used to describe the variation of sorbate breakthrough volume as illustrated in Figure 8. Utilizing the experimental apparatus described in the last section, retention volumes were measured as a function of pressure at 40°C ($T_r = 1.03$) over as wide a range of pressure as possible to permit elucidation of the breakthrough characteristics for the selected sorbates. Examination of the pulse profiles indicated a high degree of symmetry which was indicative of the absence of non-linear sorption isotherm for the systems under study. Therefore, the reported retention volume measurements can be equated with the breakthrough and/or desorption pattern of the adsorbate during its passage through the column bed.

Retention volume data were computed using Equation 2:

$$V_r = (T_{col}/T_a) (Z_a/Z_{col}) (p_a - p_{water}/p_{col}) F_a (t_r - t_o) \quad (2)$$

where V_r = retention volume of the adsorbate

T_{col} = column temperature

T_a = ambient temperature

Z_{col} = compressibility factor at p_c

Z_a = compressibility factor at ambient pressure

p_a = ambient pressure

p_{col} = column pressure

p_{water} = vapor pressure of water

F_a = ambient flow rate

t_r = retention time (peak maxima)

t_o = retention time of unretained adsorbate pulse

The retention data described by Equation 2 are corrected from ambient conditions to the prevailing temperature and pressure conditions within the sorbent column. Use of the expansion valve at the end of the chromatographic column resulted in a negligible pressure drop across the sorbent bed, thereby simplifying the pressure correction factor used in the retention volume computations (23, 39).

The retention volume computed by Equation 2, V_r , can be related to the adsorption coefficient and the surface area value of the sorbent bed by:

$$V_r = K_A A_s \quad (3)$$

where K_A = equilibrium adsorption coefficient in the Henry's Law region of the adsorption isotherm

A_s = total surface area of the sorbent bed

Unfortunately K_A values cannot be directly calculated from retention volume measurements by Equation 3 since the interfacial surface area is changing as a function of pressure due to the carbon dioxide sorption. However, the relative magnitude of the equilibrium shift of the sorbate from the solid adsorbent into the gaseous phase can be estimated by calculating the capacity factor, k' , according to Equation 4 as given below:

$$k' = \frac{V_r - V_o}{V_o} \quad (4)$$

where V_o is the column void volume.

Results and Discussion

The application of pressure causes a considerable decrease in the retention or breakthrough volume for an adsorbate transversing down a sorbent column. This trend is amply illustrated in Figure 9 where the retention volume for benzene in CO_2 has been plotted as a function of pressure for the crosslinked styrene/divinylbenzene resin at 40°C. In this figure, there is a considerable decrease initially in V_r over a small pressure interval and the breakthrough volume appears to become constant

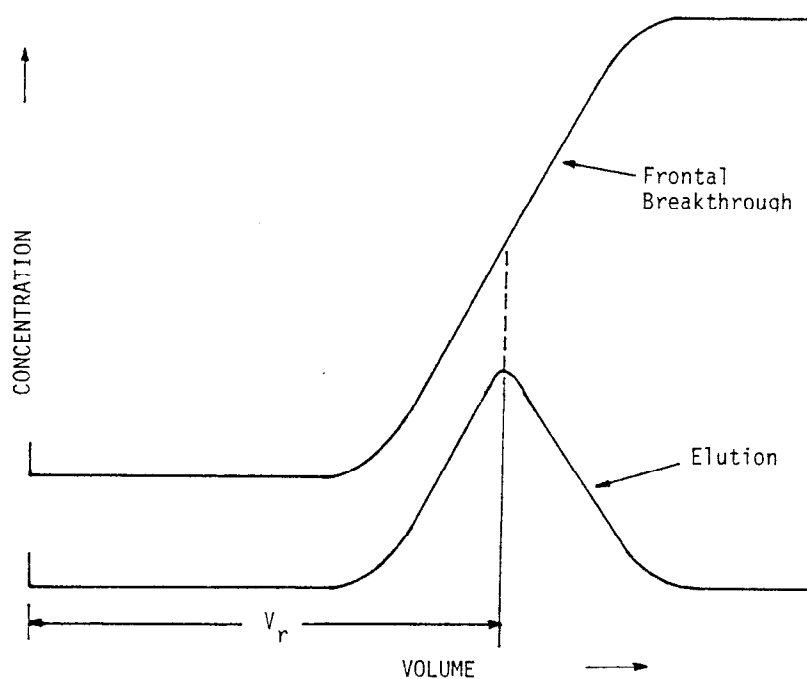


Figure 8. Relationship between the mid-point of the frontal breakthrough profile and the elution peak maxima.

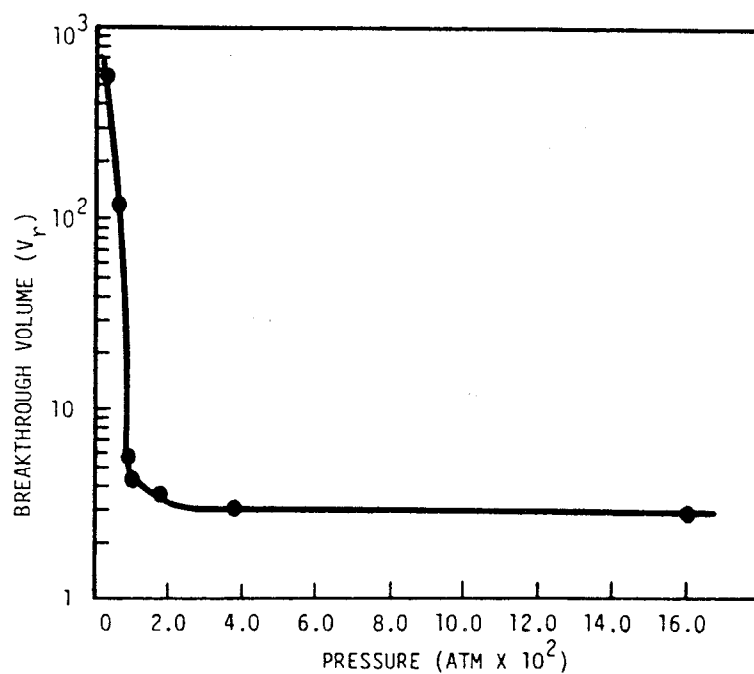


Figure 9. Breakthrough volume as a function of carbon dioxide pressure for benzene on the crosslinked polymeric resin.

beyond 200 atmospheres. The observed trend implies that further application of pressure affords no advantage in removing benzene from the adsorbent column. In general, all of sorbates studied in our experiments exhibited a similar trend upon injection into the dense CO_2 carrier gas.

Close examination of Figure 9 reveals that the rate of change for the retention volume with pressure undergoes an inflexion in the low pressure region of the graph. Therefore, additional measurements were taken to confirm this trend at pressures below 200 atmospheres. Figure 10 shows the results of this extended study for benzene on the resin adsorbent. The data show that the rate of decrease in the breakthrough volume is linear up to a pressure of approximately 70 atmospheres, however beyond this degree of gas compression, the sorbate retention volume decreases even more rapidly with increasing pressure. At a pressure below 100 atmospheres, the breakthrough volume of benzene approaches a constant value equivalent to the void volume of the column bed. Similar conclusions were reached when V_r was plotted as a function of gas density.

To confirm the above observations, an additional set of experiments were performed using a different sorbate probe, n-heptane. Once again, as with benzene, the retention volume was found to decrease in a similar manner with increasing gas pressure on the crosslinked resin sorbent. As shown in both Figures 10 and 11, the abrupt decrease in breakthrough volume occurs at a gas pressure close to the p_c or p_{max} value as calculated by Equation 1 for carbon dioxide. A similar inflection has also been noted by Sie, Van Beersum, and Rijnders (42) when the logarithm of the partition coefficient is plotted as a function of pressure in high pressure gas-liquid chromatographic studies. The above result suggests that the uptake of supercritical gas by the adsorbent produces a significant change in the breakthrough volume of the sorbate pulse and that observed migration enhancement is in part due to modification of the gas-solid interface by the dense fluid.

Similar experiments were also conducted on the styrene/divinylbenzene adsorbent in which the capacity factor and retention volumes were determined for a series of n-alkanes ($n\text{-C}_5\text{-C}_7$) at 40°C . It was found that the capacity factors for the homologues decreased linearly by an order of two magnitudes and in a parallel fashion up to a pressure of 1250 psig (85 atm.). At this pressure the solute capacity factors began to change rapidly with pressure, similar to the trend observed in the breakthrough volume for benzene and n-heptane reported above. It was also noted in this transition region, that the capacity factors for the individual alkanes tended to merge together, and that differential migration down the column was not possible in this higher pressure regime. Such a result suggests that fractionation of the above homologues can only be accomplished successfully below the p_{max} value associated with the adsorption of the critical fluid at the gas-solid interface. Apparently, the formation of a multi molecular layer of adsorbed gas with increasing pressure not only assists in desorbing the injected sorbate but significantly nullifies the potential field of the adsorbent to such an extent that differential

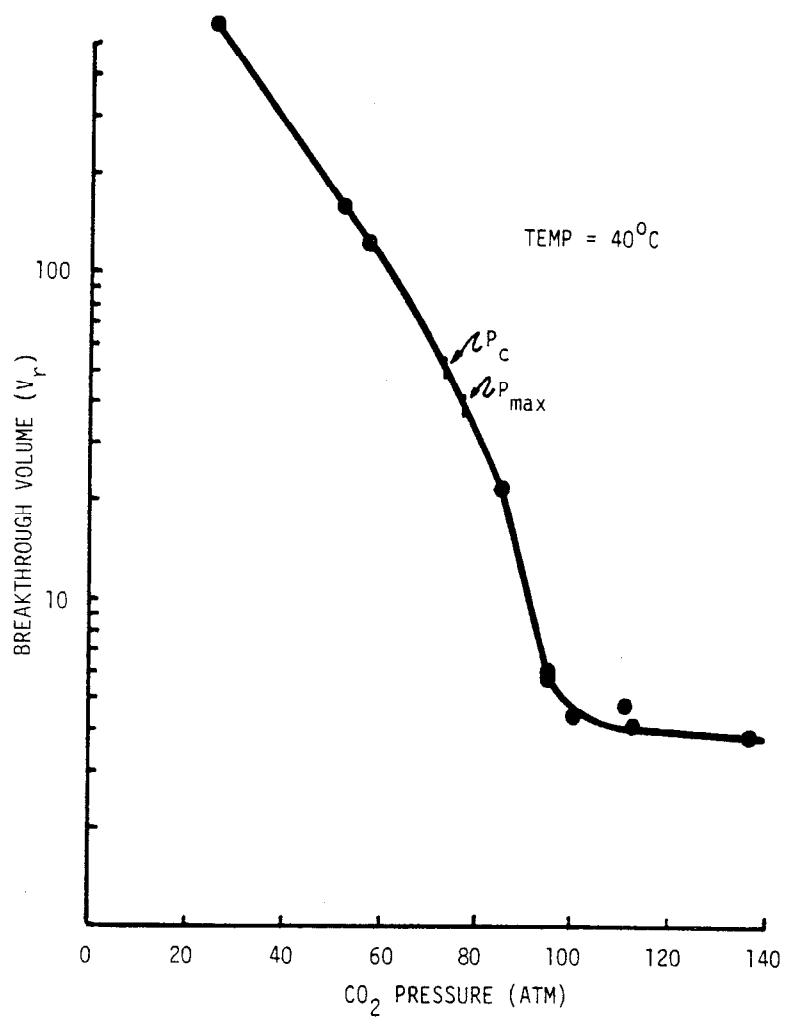


Figure 10. Retention volume for benzene versus carbon dioxide pressure on the styrene/divinylbenzene resin.

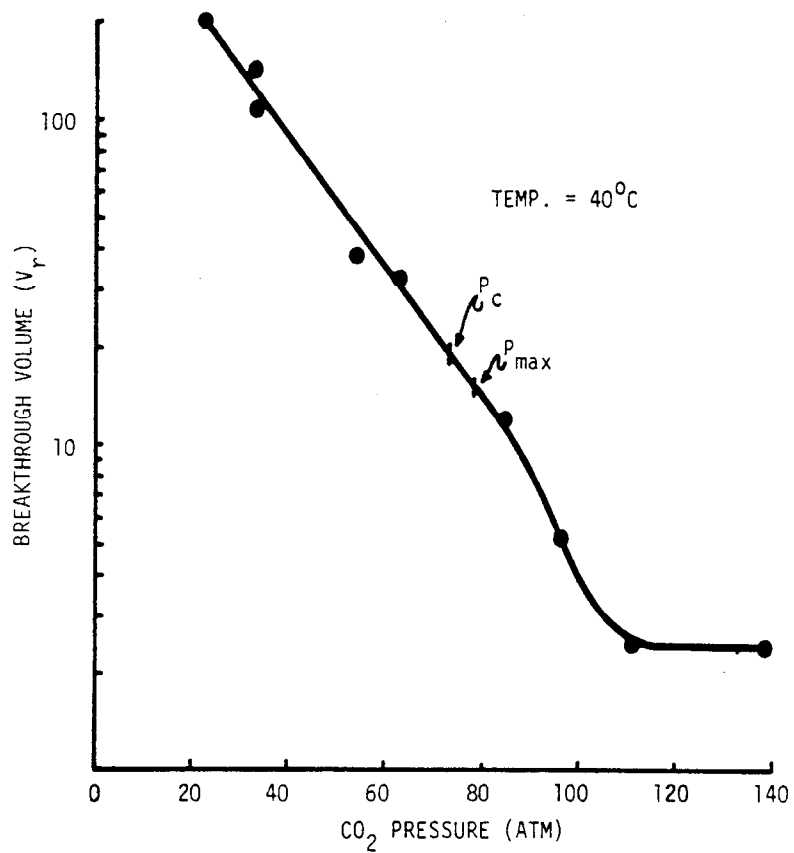


Figure 11. Retention volume for n-heptane as a function of carbon dioxide pressure on the styrene/divinylbenzene resin.

adsorption of various adsorbates is no longer possible. Similar conclusions have been reached by other investigators (43) using elution chromatographic experiments.

Additional evidence for the role of the supercritical fluid in modifying the interface is provided in Figure 12. Here the capacity factor for n-pentane on alumina at 40°C is shown as a function of pressure up to 700 atmospheres. The considerable reduction in k' below 100 atmospheres parallels the solute breakthrough behavior described earlier on the organic resin. Also plotted in Figure 12 is gravimetric adsorption data for three gases adsorbing on alumina; carbon dioxide, nitrogen, and carbon monoxide, as taken from the literature. The isotherm depicted for nitrogen and carbon monoxide were abstracted from the study of Menon (44) and represent the differential adsorption of these gases at 50°C. The maximum sorption of CO₂ on alumina is designated with an asterisk in Figure 12 for clarity, however the entire isotherm can be found in the paper of Ozawa and Ogino (33). The actual isotherm for CO₂ on alumina at 40°C is quite sharp when compared to the nitrogen and carbon monoxide isotherms, a feature in keeping with the low reduced temperature at which the CO₂ is adsorbed ($T_r = 1.03$). The adsorption recorded for nitrogen and carbon monoxide was taken at reduced temperatures of 2.48 and 2.35, respectively, hence additional gas compression is required to achieve maximum uptake of the supercritical fluid. Despite the different aluminas used in the cited experimental studies, the gravimetric adsorption data in Figure 12 suggest that the breakthrough volume is controlled by competitive adsorption of the supercritical fluid at the gas-solid interface. The close proximity of the carbon dioxide adsorption maximum to the region of maximum change in V_r supports the above concept. Likewise, the higher pressures required to reach the adsorption maximum in the CO and N₂ cases, would argue that a more gradual change in the breakthrough volume with pressure should occur for similar sorbates which are desorbed at 50°C using these supercritical fluids. Maximum desorption due to competitive adsorption of the supercritical fluid at the gas-solid interface is achieved by operating close to the critical temperature or p_{max} of the displacing gas.

To test the above concept, a rather radical experiment was performed employing helium as the carrier gas at 40°C ($T_r = 59.1$) with subsequent measurement of the retention volumes for several light hydrocarbons (n-C₃-C₅) on the alumina column. Figure 13 shows the reduction in the capacity factor with pressure for n-butane as a sorbate utilizing helium and carbon dioxide as carrier gases. The trend observed in the capacity factor for n-butane as well as the other alkanes in pressurized carbon dioxide is identical to that observed with alkanes of higher carbon number on alumina and the crosslinked organic resin. However, when helium is used as the carrier fluid, there appeared to be a small initial drop in the capacity factor followed by a more gradual decrease in k' with increasing pressure (up to 10,000 psig). Examination of Figure 13 suggests that much higher pressures must be employed to effect a further reduction in the breakthrough volume for n-butane in helium on the oxide sorbent, at least comparable to that observed when using carbon

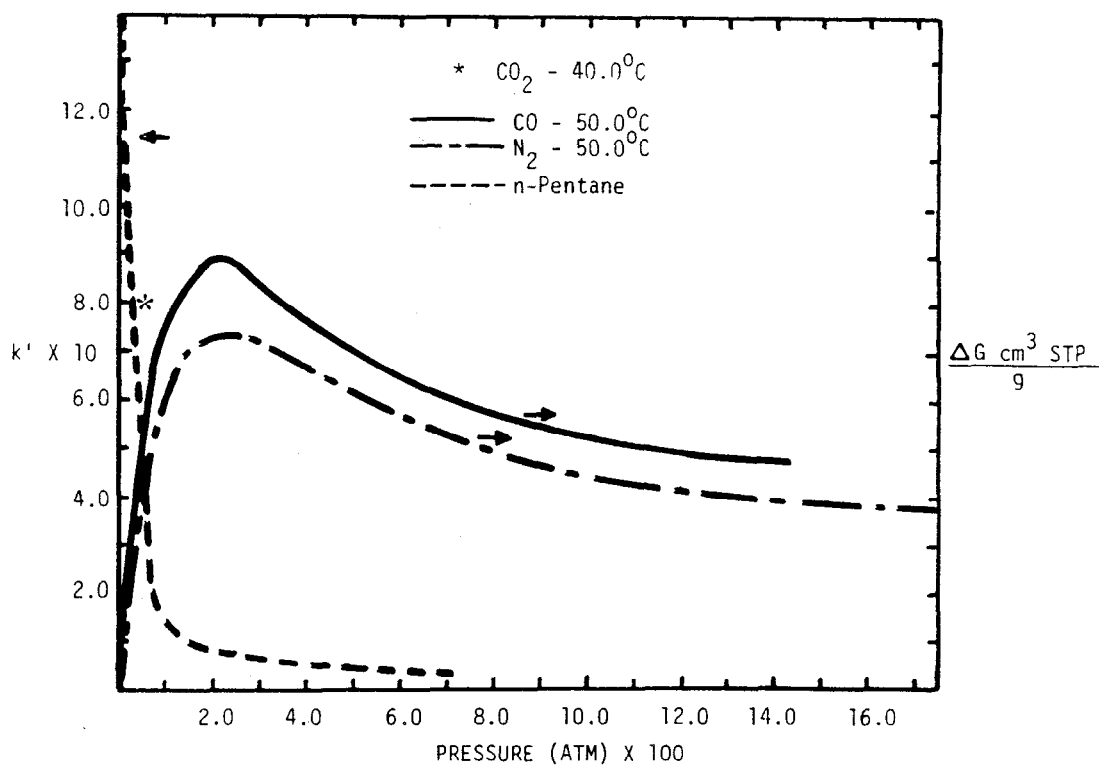


Figure 12. Capacity factor for n-pentane on alumina column at 40°C and the differential adsorption of three gases as a function of gas compression.

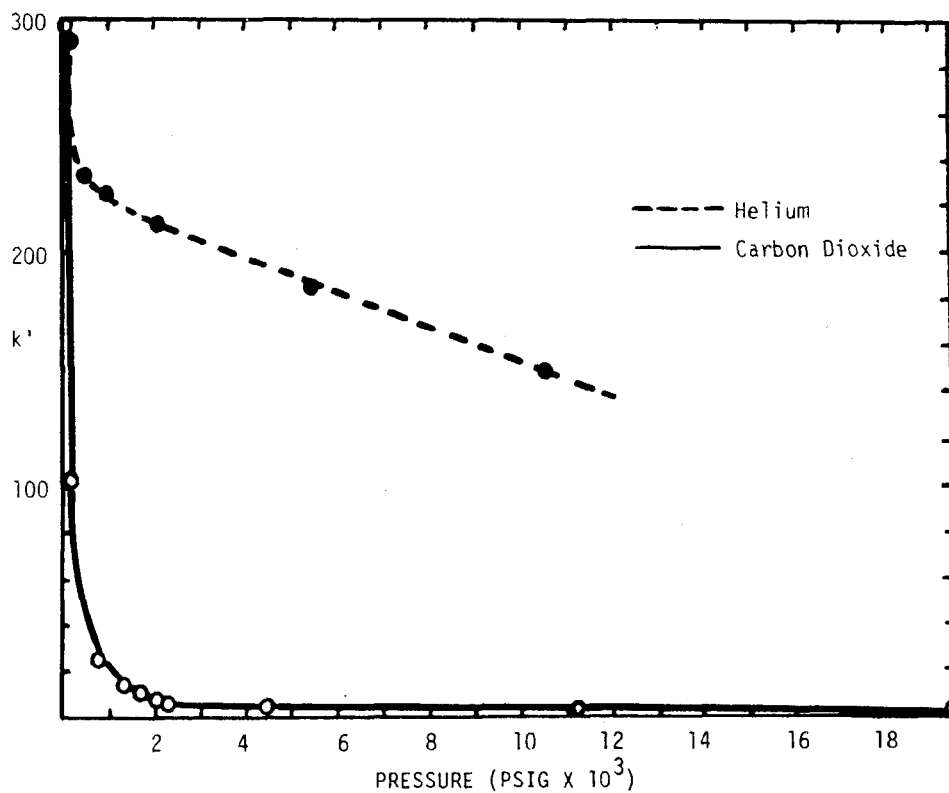


Figure 13. Capacity factor for n-butane in carbon dioxide and helium as a function of column pressure. Temp. = 40°C .

dioxide as the supercritical fluid phase. We believe that the observed difference in sorbate behavior in the two candidate gases is a reflection of the degree of surface modification caused by the different amounts of adsorption exhibited by the two supercritical gases. Sorption of helium at such a high reduced temperature is very low, but not entirely negligible at the pressures employed in this study. This later factor combined with the weak solvent power of helium gas [the solubility parameter for helium at 14,000 psig is 1.6 Hildebrands (45)] most likely accounts for the recorded gradual breakthrough of the n-butane pulse from the alumina column.

Conclusions

In this study, we have examined the role of a supercritical fluid adsorbing at the gas-solid interface and the possible implications of such a phenomena on adsorption/desorption processes. The above results strongly support the hypothesis that displacement of a bound adsorbate via competitive adsorption of the supercritical fluid at the interface is a major factor in regenerating adsorbents and in controlling the partition of the solute (sorbate) into the fluid phase. Additional support for this concept can be found in the regeneration studies of Eppig and co-workers (14) who demonstrated the recovery of ethanol, methyl ethyl ketone, and toluene from activated carbon beds using modest CO₂ pressures (less than 100 atms.). Adsorption/desorption studies of light hydrocarbon/CO₂ mixtures on molecular sieve (46) also indicate that CO₂ is preferentially adsorbed over the alkane moieties, supporting a similar concept advanced in this study.

The retention volume data presented in this study imply that there are distinct regions of sorbate breakthrough behavior that are in part defined by the extent of compressed gas adsorption at the solid interface. The region for most profitable fractionation of adsorbates would appear to lie below the p_{\max} value as defined by the adsorption isotherm of the supercritical fluid. Plots of retention volume versus pressure also are of great aid in defining a maximum pressure beyond which no further reduction in breakthrough volume is possible through increased gas compression. Such data is of value in specifying the most efficient conditions for the rapid and economical supercritical fluid regeneration of adsorbent beds. It would appear that the p_{\max} value discussed above, is a minimal pressure which investigators should endeavor to attain when attempting to desorb compounds with supercritical fluid media. However, extra gas compression may be required above the p_{\max} value to solvate and strip strongly adsorbed components from p_{\max} adsorbent matrix. Additional experimental studies should be undertaken in the future to better define and verify the concepts presented in this study, particularly utilizing other supercritical fluid displacing agents and adsorbates of lower volatility and a polar nature.

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